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13. ABSTRACT *(Maximum 200 words)*

A substantial number of new polymer systems have been synthesized and developed to make use of the valuable properties imparted by inorganic elements incorporated into a macromolecular structure. The new polymers range from solvent-resistant elastomers to non-burning materials, and species that form excellent membranes and structural materials. The work has led also to the development of a system for understanding the relationship between polymer structure and useful property combinations in ways that should assist the rapid evolution of new polymers needed for specific specialized applications.

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Polymers, materials, polyphosphazenes, elastomers, membranes, composites, and fire-resistant materials

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THE SYNTHESIS AND STRUCTURE OF POLYPHOSPHAZENES

Final Report for Period May 1, 1991 - April 30, 1994

U. S. Army Research Office

DAAL03-91-G-0124
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Problem Studied:

The purpose of this program was the design and exploration of chemical synthesis routes to new polymers with special combinations of properties. The emphasis was on new elastomers and fire-retardant materials, new polymeric composite materials, and polymers for use in membranes.

Summary of the Most Important Results:

Numerous new polymers have been prepared that have backbones of phosphorus and nitrogen atoms with or without carbon or sulfur as co-skeletal elements, and with side groups that range from complex aryloxy units to electroactive species such as pyrrole, thiophene, or furan groups, and from amino groups to organometallic units. These polymers have been fully characterized and their special properties studied.

A new class of polymers--the poly(phosphazophosphazenes)--have been developed. The high loading of phosphorus and nitrogen in these materials underlies their importance as possible flame-resistant and flame-retardant polymers.

A series of new membrane materials for gas separations has been developed and studied. One of these membranes has a very high permeability to oxygen and may have prospective uses in both gas separations and protective clothing.

Other polymers have been studied for the selective complexation of metal ions and are prototypes for hazardous waste management devices.

Finally, several new series of polymer blends and interpenetrating network systems have been developed using polyphosphazenes as one of the components to confer flame-resistance or impact-resistance on the materials.

Significance:

The significance of this research has been recognized by two American Chemical Society awards to the principal investigator during the past two years--the 1992 ACS Award in Materials Chemistry and the 1994 ACS Herman Mark Award in Polymer Science.

Manuscripts Based on this Work Submitted or Published (5/1/91 - 4/30/94):

"Preparation and Characterization of Poly(organophosphazene) Blends
H. R. Allcock and K. B. Visscher
Chemistry of Materials **1992**, 4, 1182-1187.

"Strained Inorganic Heterocyclic Compounds and Their Conversion to Macrocycles and High Polymers"
H. R. Allcock
Chapter in *The Chemistry of Inorganic Ring Systems* (R. Steudel, ed.)
Elsevier: Amsterdam, **1992**, 145-169.

"Synthesis of Poly(bis-phosphazo)phosphazenes Bearing Aryloxy and Alkoxy Side Groups"
H. R. Allcock and Dennis C. Ngo
Macromolecules **1992**, 25, 2802-2810.

"Polyphosphazenes"
H. R. Allcock
J. Inorg. and Organomet. Polymers **1992**, 2, 197-211.

"The Synthesis and Molecular Structures of Cyclic and Short-Chain Linear Phosphazenes Bearing o-Dichlorophenoxy and o-Dimethylphenoxy Side Groups"
H. R. Allcock, D. C. Ngo, M. Parvez, and K. B. Visscher
J. Chem. Soc. **1992**, 10, 1687-1699.

"Polyphosphazenes Bearing Polymerizable Pyrrole, Thiophene, and Furan Side Groups: Synthesis and Chemical Oxidation"
H. R. Allcock, J. A. Dodge, L. S. Van Dyke, and C. R. Martin
Chemistry of Materials **1992**, 4, 780-788.

"Cyanophosphazene Small Molecules and High Polymers: Synthesis and Structure"
H. R. Allcock, J. S. Rutt, M. F. Welker, and M. Parvez
Inorganic Chemistry **1993**, 32, 2315-2321

"Ring-Opening Polymerization in Phosphazene Chemistry"
H. R. Allcock
Chapter in *Ring-Opening Polymerization* (D. J. Brunelle, ed.)
Hansers Publishers: Munich, Germany, **1993**, pp. 217-327.

"Poly(thiophosphazenes): New Inorganic Polymers"
H. R. Allcock, J. A. Dodge, and I. Manners
Macromolecules **1993**, 26, 11-16.

"The Polymerization Behavior of Pentachlorocyclo(carbotriphosphazene), $N_3P_2CCl_5$"
S. M. Coley, H. R. Allcock, I. Manners, K. Visscher, M. Parvez, O. Nuyken, and G. Renner
Polym. Prepr. (ACS Div. Poly. Chem.) **1993**, 33 166-167

"Gas Permeation and Selectivity of Poly(organophosphazene) Membranes"
H. R. Allcock, C. J. Nelson, W. D. Coggio, I. Manners, D. Walker, L. Pessan, and W. J. Koros
Macromolecules **1993**, 26, 1493-1502

"Synthesis and Characterization of Metallophosphazene Derivatives: Solution State and Surface Reactions"
H. R. Allcock, E. N. Silverberg, C. Nelson, and W. D. Coggio
Chemistry of Materials **1993**, 5, 1307-1314.

"Cyanophosphazene Small Molecules and High Polymers: Synthesis and Structure"
H. R. Allcock, J. S. Rutt, M. F. Welker, and M. Parvez
Inorganic Chemistry **1993**, 32, 2315-2321.

"Reactivity and Polymerization Behavior of Pentachloro(carbotriphosphazene), $N_3P_2CCl_5$"
H. R. Allcock, S. M. Coley, I. Manners, K. B. Visscher, M. Parvez, O. Nuyken, and G. Renner
Inorganic Chemistry **1993**, 32, 5088-5094.

"Synthesis and Structures of (*p*-Halogenophenoxy)phosphazenes: Comparison of the Stuctures of Cyclic and Linear Short-Chain Species"
H. R. Allcock, D. C. Ngo, M. Parvez, and K. B. Visscher
Inorganic Chemistry **1994**, 33, 2090-2102

"Inorganic-Organic Polymers and their Role in Materials Science"
H. R. Allcock
Advanced Materials **1994**, 6, 106-115

"Synthesis of Cyclo- and Polyphosphazenes with Pyridine Side Groups"
U. Diefenbach and H. R. Allcock
Inorganic Chemistry (in press)

"Extrusion of Nitriles from Carbophosphazenes to Yield Classical Phosphazenes, and the Reverse Reaction"
S. M. Coley and H. R. Allcock
J. Am. Chem. Soc. (submitted)

"Synthesis and Properties of Poly[amino(carbophosphazenes)]"
H. R. Allcock, S. M. Coley, and C. T. Morrissey
Macromolecules (submitted)

"Poly(organophosphazenes) Containing Allyl Side Groups: Cross-linking by Hydrosilylation"
H. R. Allcock, D. E. Smith, Y. B. Kim, and J. Fitzgerald
Macromolecules (submitted)

"Synthesis and Characterization of Ion-Complexing Polyphosphazene Interpenetrating Polymer Networks"
H. R. Allcock and K. B. Visscher
Chemistry of Materials (submitted)

"Poly(monophosphazo)phosphazenes: New Polymers with $N{=}PR_3$ Side Groups"
H. R. Allcock, S. E. Kuharcik, C. T. Morrissey, and D. C. Ngo
(submitted)

"Cross-Linking Reactions for the Conversion of Polyphosphazenes into Useful Materials"
H. R. Allcock
Chemistry of Materials Review (submitted)

Patents Issued During this Funding Period:

"Polycarbophosphazenes"
H. R. Allcock, I. Manners, G. Renner, and O. Nuyken
U.S. Patent 5,093,438 (1992) (assigned to The Pennsylvania Research Corporation)

"Method for Forming Polythiophosphazene Macromolecules"
H. R. Allcock, J. A. Dodge, I. Manners, G. Renner, and O Nuyken
U.S. Patent 5,101,003 (1992) (assigned to The Pennsylvania Research Corporation)

Technical Progress Reports:

Period Covered:

(1) May 1, 1991 - December 31, 1991
(2) January 1, 1992 - June 30, 1992
(3) July 1, 1992 - December 31, 1992
(4) January 1 - December 31, 1993

Scientific Personnel Supported by this Project and Degrees Awarded 5/1/91-4/30/94:

Harry R. Allcock (principal investigator)
Young Baek Kim (postdoctoral fellow)
Dennis C. Ngo (Ph.D. 1991, now a research scientist with 3M)
Jeffrey A. Dodge (Ph.D. 1992, now a research scientist at Miles/Bayer Co.)
Karyn B. Visscher (Ph.D., 1993 and now postdoctoral fellow in group)
Suzanne M. Coley (Ph.D, 1993, now a research scientist with Shipley Co.)
Constance J. Nelson (Ph.D. 1993, now a research scientist with 3M)
Christopher T. Morrissey (graduate student)
Eric H. Klingenberg (graduate student)
Carey Reed (graduate student)